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Crystalline silica in heated man-made vitreous fibres: A review

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ABSTRACT

Refractory ceramic fibres (RCF) and alkaline earth silicate (AES) wools are types of man-made vitreous fibre (MMVF) that are used in demanding high-temperature industrial applications, generally above 900 °C and up to 1400 °C. When exposed to prolonged high temperatures, MMVF can devitrify with the formation of cristobalite and other crystalline silica species, which is of potential concern because crystalline silica (CS) is classified as carcinogenic. This article reviews the chemico-physical processes and morphological consequences of fibre devitrification, the forms and micro-location of CS produced, and the toxicity of devitrified fibres and the CS species formed in this way. It also examines scenarios for worker exposure to the products of fibre devitrification in industries using RCF and/or AES wools. We identify gaps in knowledge and make recommendations for future research.

1. Introduction

Man-made vitreous fibres (MMVF) – part of the wider group of man-made mineral fibres (MMMF) – are used extensively in commercial and residential buildings for both thermal and sound insulation purposes, and in certain more specialist products such as gaskets and filters. High temperature insulation wools (HTIW), used mostly in demanding high temperature industrial applications, comprise three main groups: refractory ceramic fibres (RCF; or alumina-silicate wools, ASWs) and alkaline earth silicate (AES) wools, both of which are MMVFs, plus polycrystalline wools (PCWs), which are non-vitreous MMMF.

RCF/ASWs are amorphous fibres produced by melting a combination of alumina (Al_2O_3) and silicon (SiO_2) (in approximate 50:50 proportions), with or without added zirconium. Products made from RCF/ASWs are generally used at application temperatures >900 °C (in the range 600–1400 °C) in industrial equipment like furnaces and kilns with critical application conditions, in fire protection and in automotive exhaust systems. They also are highly resistant to chemical attack. RCFs have been classified by the International Agency for Research on Cancer (IARC) as *possibly carcinogenic to humans* (*Group 2B*) (IARC, 2002).

AES wools consist of amorphous fibres produced by melting a combination of oxides of calcium, magnesium and silicon. These wools are generally used at application temperatures up to 1200 °C in continuously operating equipment. The fibre properties can be adjusted by varying the quantity and type of alkaline-earth content for different applications. Products made from AES wools are generally used in industrial equipment, fire protection, automotive exhaust systems and domestic appliances. AES wools are not classified as carcinogenic and are therefore sometimes used as an alternative to RCF/ASW when operational conditions allow.

PCWs, manufactured using a sol–gel process, consist of crystalline fibres containing more than 70 wt% Al_2O_3, with the remainder consisting predominantly of SiO_2. They are generally used at application temperatures greater than 1300 °C, or in demanding thermo/mechanical applications, typically as support mats in catalytic converters and diesel particulate filters, and as insulation in industrial high temperature furnaces, particularly in high temperature and/or chemically aggressive environments. Because by their nature PCWs are already partially or wholly crystalline and contain no CS species, they are not considered further in this review.

When exposed to prolonged high temperatures, it is known that RCFs can devitrify, or crystallize, with the formation of cristobalite, a type of crystalline silica (CS) (Butler and Dyson, 1997; Dyson et al., 1997; Maxim et al., 1999; Brown, 2000; Comodi et al., 2010). This devitrification process is of potential concern because CS is classified as carcinogenic to humans (IARC, 2012), and workers involved in the removal of RCF insulation in high temperature furnaces may be occupationally exposed to it. Moreover, there is the possibility that other MMVFs used as HTIWs may degrade in a similar way (as identified by Comodi et al., 2010), which would likewise be of potential concern.

This review constitutes a thorough review of the literature with the aim of providing a full understanding of the devitrification process in RCF/ASW and other MMVFs, the exact forms of CS produced and the toxicity of the crystallised fibres thus produced.

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Table 1
Summary of fibre exposure conditions and resulting surface structures and devitrification products.

Fibre grade	Furnace exposure conditions		Fibre surface structure		Devitrification products
	Temp (°C)	Time (weeks)	Microstructure	Material	
Standard	–	–	Smooth	Glassy	None
	1200	8	Sub-micron crystallites	Mullite	Cristobalite, mullite
	1400	0.5	Smooth	Largely glassy	Mullite, β-cristobalite (tr.)
High-duty	–	–	Smooth	Glassy	None
	1200	2	Sub-micron crystallites	Mullite	β-Cristobalite, mullite
	1400	2	Micron crystallites in silica 'sea'	Mullite & glassy silica	Mullite, β-cristobalite (tr.)
Zirconia	–	–	Smooth	Glassy	None
	1200	1	Sub-micron crystallites	?	Mullite, β-cristobalite, zirconia (tetr.)
	1400	8	Near-micron crystallites	?	Mullite, β-cristobalite, zircon

tr., trace; tetr., tetragonal. From: Brown et al. (1992).

Note: The papers reviewed here used various different descriptions and acronyms for the fibre types investigated, details of which are given in Supplementary Table 1.[1]

2. The physical chemistry of devitrification

Devitrification, by definition, is the conversion of glassy matter into a stony mass by heating and slow cooling, the result being the formation of crystallites, microbites, etc., in the glass base, which are then called devitrification products. Over a number of years, MMVFs of various types have been experimentally subjected to heat treatment, over varying time periods, and the processes and products of devitrification recorded. The general consensus is that when fibres are heated there is a varying degree of crystallisation of the fibres, and also variation in the devitrification products so formed, depending on the composition of the original amorphous fibre. The degree of devitrification is dependent both on the temperature to which the fibre is heated and the length of time this temperature is maintained. Heating fibres to very high temperatures (well above their recommended use temperature) for short periods leads to similar levels of devitrification as heating fibres at lower temperatures for longer periods. Prolonged periods of exposure of RCFs to extremely high temperatures, in the region of 1300 °C, are known to lead to the formation of mullite (an aluminosilicate crystalline compound ($Al_6Si_2O_{13}$) and CS, in the form of cristobalite, and other crystalline products (Gualtieri et al., 2009).

The phases and phase changes that occur in RCFs as a function of temperature have been discussed in detail by Brown et al. (1992), and are summarised in Table 1. These authors examined the composition, structure and biological activity of fibres at room temperature in the 'as manufactured' state, and following heating to 1200 and 1400 °C for differing times. They focused on a 'standard' and a 'zirconia grade' fibre that were available and commonly used at the time, and a 'high-duty' grade that was extensively used until its withdrawal from the market. The high-duty grade materials had a higher classification temperature (1400 °C) than the standard grade materials (1260 °C). Heating all three fibres to 1200 °C resulted in the initial formation of mullite crystals on the surface, and of cristobalite in the standard grade fibres and β-cristobalite in the case of the high-duty and zirconia products. When all three products were heated to 1400 °C mullite and β-cristobalite were formed, although the length of time it took was different between the fibre grades.

Prior to this study, conflicting results had been observed. Sopicka-Lizer and Pawlowski (1980) heated a RCF up to about 1500 °C (at 7 °C/min), but only observed the formation of mullite at about 971 °C. Vine et al. (1984) ground a bulk fibre (that contained small quantities of oxides of iron, titanium [TiO_2] and calcium) to a fine powder, and heated it for 5 weeks at 1150 °C. They observed that crystallisation to cristobalite and mullite had taken place; the conversion to mullite was rapid and took place within hours, while the conversion to cristobalite took a few weeks. Gantner (1986) took RCF samples from a furnace (prior to removal) and demonstrated that the majority of devitrification occurred on the surface layers of the hot face, and that at over four inches from the furnace surface cristobalite was not found, the percentage decreasing exponentially with depth. This was attributed to a possible temperature threshold for cristobalite formation, which the authors estimated to be about 930 °C based on the maximum furnace set-point of 1315 °C.

Karlsson et al. (1986) tested two samples of 'cerafiber' (47% Al_2O_3; 52.7% SiO_2); one had been heated to 1200 °C over 600 firing cycles, the other to 1150 °C over 425 cycles. Relatively little cristobalite was observed in the first fibre, whereas a significant amount was observed in the second. A significant amount of cristobalite was also observed in 'cerachrome' fibres (43.5% Al_2O_3; 53.5% SiO_2; 2.75% Cr_2O_3) that had been heated to 1200 °C over 600 cycles. The amount of the crystalline phases, mullite and cristobalite, formed depended on the fibre composition; higher Al_2O_3 content resulted in the formation of mullite as the main phase. Temperature was also important, with mullite forming at lower temperatures than cristobalite. Fibres closest to the surface of the furnace completely crystallised; however, the cristobalite content was at a maximum about 25 mm from the hot face.

Holroyd et al. (1988) heated a standard grade RCF blanket to between 950 and 1155 °C for 29 days, and a high-duty grade blanket to between 1100 and 1270 °C for 33 days.[2] Dust released from exposed blankets contained cristobalite, mullite and a vitreous phase. The cristobalite formed at temperatures above a threshold of about 1080 °C in both grades of blankets. For the standard blanket (3.7 cm thick), cristobalite decreased from about 10% at the hot face to zero at a depth of 1.2 cm; whilst in the high-duty blanket (2.5 cm thick) cristobalite decreased from about 20% at the hot face to about 2% at the cold face.

Zhen and Song (1990) examined the thermal degradation of four different RCFs, noting that all remained in a glassy state up to 800 °C but that at 1100 °C a small quantity of cristobalite formed, and that generally the quantity of crystallised cristobalite was proportionate to the SiO_2 content of the RCFs. The authors stated that the temperature at which cristobalite appeared was 1100 °C in fibres heated for a long duration (500 h), but was 1200 °C in fibres heated for a short time (8 h).

Since 1992 there have been a number of other studies that have

[1] *Note:* The fibre descriptions/constituents given in this table are as presented by the respective authors and are not necessarily correct (e.g. see Harrison and Brown (2011)).

[2] *In situ* cold-face and hot-face temperatures.

similarly shown varying results. Laskowski et al. (1994) took samples from RCF blankets and exposed them to selected temperatures between 600 and 1500 °C, for 2 1/2 min to 7300 h and demonstrated that the thresholds for the formation of both mullite and cristobalite occur at lower temperatures following longer exposure times. The threshold of cristobalite formation decreased with temperature from 1500 °C at 2½ min exposure to 900 °C after 43 weeks.

Butler and Dyson (1997) quantified the levels of different forms of cristobalite in devitrified RCFs. Heating standard RCF at 1500 °C for 48 h resulted in the formation of three crystalline phases that were stable at room temperature: mullite, α-cristobalite, and a second form of cristobalite termed α′-cristobalite. Heating for longer times promoted the formation of increasing amounts of α-cristobalite, and decreasing amounts of α′-cristobalite. In follow-up work, Dyson et al. (1997) studied the devitrification process in cubes (5 cm^3) of five common grades of RCF insulation, heated between 1050 and 1500 °C, for up to 4004 h. CS was present in all heated samples, mostly in the α′-cristobalite form, and only as α-cristobalite after long periods of heating at high temperatures. The rate of devitrification was rapid in all fibre types at 1300 °C and after 374 h virtually all amorphous material had been converted to the crystalline phase; at 1500 °C devitrification was essentially complete after 48 h.

Binde and Bolender (2002) examined the formation of cristobalite when four different AES fibres and two RCFs were heated. The formation of cristobalite varied between fibre types; no data were presented for the RCFs, but the authors claimed a correlation between cristobalite content and the silica composition of the fibre.

Bhattacharyya et al. (2005) examined the devitrification characteristics of commercially available standard grade RCFs, heating the fibres for 1–4 h at 1100, 1250 and 1350 °C. Results indicated progressive mullite development with time and temperature; also the samples gave rise to an extraneous phase at the higher temperatures that the authors suggested was probably a devitrified product of the high temperature heat treated fibre, but they did not confirm it was cristobalite.

Tonnesen and Telle (2007) heated a series of AES fibres and RCFs to between 1050 and 1250 °C for 24–500 h, noting that cristobalite formed when the AES fibres were heated to 1050 °C and above. For magnesium-silicate fibres, formation rose from 1% after 24 h up to nearly 25% after 100 h; higher temperatures led to higher values between 27% and 33% after 24 h. The high amounts of cristobalite were expected as a consequence of the high SiO_2 composition. For the AES fibres the temperature range for recognisable cristobalite formation lay between 1050 and 1100 °C. Cristobalite formation in these fibres became even more evident after 100 h at 1100 °C, when the cristobalite content increased by up to 11%. For RCF1260 and RCF1400, relatively small amounts of cristobalite were formed at temperatures below 1250 °C. The presence of zirconium oxide (ZrO_2), in RCF1430Z, led to crystal phases of cristobalite after 24 h at 1250 °C, up to a quantity of 11% by weight.

Gualtieri et al. (2009) examined the thermal transformation of a number of MMVFs with maximum operational working temperatures ranging from 600 to 1300 °C, to determine whether they could be safely recycled as secondary raw materials (SRMs). Powdered samples were pressed into test pieces of about 0.25 cm^3, and heated from room temperature to 1600 °C at a rate of 10 °C/minute, for 72 h, although the exact thermal runs varied between fibres. The RCF and AES fibres devitrified into different substances at different temperatures, the RCF to mullite and cristobalite between 900 and 1000 °C, and the AES fibre to diopside. The authors stated that the RCF could not be safely regarded as a SRM because of high cristobalite levels, concluding that the results suggested cristobalite is formed at temperatures greater than 1200 °C, and their use as insulators should be limited to lower temperatures.

Comodi et al. (2010) thermally treated unused samples of five RCFs in a laboratory furnace reaching temperatures of 1600 °C for variable times from 24 h up to 360 h. Treatment of one RCF at 950 °C for up to 1 week only resulted in the production of mullite; however, when the temperature was increased to about 1350 °C, cristobalite began to appear after 24 h, and increasing the temperature led to a further reduction of the amorphous content with an increase in cristobalite. Treatment of the Zr-RCF at 1200 °C for 24 h resulted in the complete crystallisation of the fibre, with significantly strong XRD peaks ascribable to cristobalite, along with peaks for mullite and zirconia. After heating 'Ecofiber' (an AES wool) up to 1200 °C, the onset of cristobalite formation was observed after 3 days, with complete crystallisation occurring after two weeks when the composition was: diopside – 85.99%; cristobalite – 9.40%; and tridymite – 4.61%.

In summary, a number of studies have investigated crystalline phases and phase-changes in heated MMVF, and the physicochemistry of devitrified fibres. There is general consensus that when fibres are heated there is a varying degree of crystallisation of the fibres depending on the composition of the original amorphous fibre. Generally, with RCF/ASW, mullite is first formed at around 980 °C, and cristobalite around 1100 °C; some MMVF also or alternatively produce diopside and β-cristobalite. The degree of crystallisation is temperature and time dependent; heating fibres to very high temperatures (above the recommended use temperature) for short periods leads to similar levels of devitrification as heating fibres at lower temperatures for longer periods. The amount of cristobalite and other CS species measured in heat-treated fibres is highly variable among studies, even for similar grades of fibre. This is probably due to inconsistency between the methods used in the various studies, including the variability in the temperatures to which the fibres were heated (1100–1500 °C), the length of time fibres were maintained at these temperatures (1 min to 120 days), the preparation of the fibres for analysis (whether they were ground or not), and the variability in chemical composition of the original fibre. Also, the amount of fibre tested was not always specified. All of these factors may have impacted on the specific results obtained. A summary of results on cristobalite formation in the above studies is given in Supplementary Table 2.

3. Morphological consequences of devitrification

Because of their non-crystalline, amorphous structure, MMVFs tend to fracture transversely, creating shorter fibres of the same diameter (NIOSH, 2006). This contrasts with asbestos fibres which have a crystalline structure and tend to fracture along the longitudinal plane under mechanical stresses, resulting in more fibres with the same length but smaller diameters. It has been suggested that these differences in morphology (including the fact that MMVF fibres are of generally much larger diameter than asbestos fibres) and cleavage patterns mean that working with MMVFs is less likely to generate high concentrations of airborne fibres than working with asbestos (NIOSH, 2006). It is important therefore to consider the effects of heating on fibre morphology as well as on chemistry. Comodi et al. (2010) showed strong fragmentation of heated fibres along the transverse axis while the diameters remained nearly unchanged. Gualtieri et al. (2009) demonstrated that RCF heated to 1300 °C was characterised by a decreased diameter (4–3.1 μm) and decreased length (77–57 μm), and a rough surface due to the presence of submicron crystals of mullite and cristobalite. Ziemann et al. (2013) have also demonstrated marked

morphological changes in AES wools following heat treatment, with significant reductions in mean fibre length.

4. Toxicity of devitrified fibres

With the exception of RCF, HTIWs are not considered to be carcinogenic, but CS is a classified carcinogen (*vide infra*) (IARC, 2002). Carcinogenicity studies of simulated after-service fibres have been carried out on rats exposed by inhalation, intrapleural infusion or intraperitoneal injection. Rossiter and Chase (1995) and Mast et al. (1995a,b), report on studies in which Fischer 344 rats were exposed to an after-service RCF (heated to 2400°F for 24 h), through inhalation, to 30 mg/m^3 of fibre for 6 h/day, 5 days/week for 24 months. This fibre was observed to contain approximately 27% free CS. At this high dose interstitial fibrosis did not appear until 12-months, whereas for the other fibres tested fibrosis was observed after 6-months. The number of tumours following exposure to the after-service fibre (RCF4) was small and not significantly different from controls exposed to untreated air, whereas following exposure to the other fibres tumour numbers were significantly increased. Pleural mesotheliomas were observed in rats exposed to all fibres, but only in one RCF4-exposed rat. RCF4 fibres were shorter (about 34% between 5 and 10 μm) and thicker (about 35% <0.5 μm) than those of RCF1, RCF2 and RCF3 and resulted in lower lung burdens of fibres longer than 20 μm (Mast et al., 1995a). Overall, in terms of lung tumour and mesothelioma induction, these studies suggested that the after-service fibres are considerably less toxic than unheated RCFs. Although this reduced toxicity may have resulted from changes in fibre length, there was certainly no indication that devitrification (and associated CS formation) rendered them any more toxic than the inhaled fibres.

Two studies that directly administered after-service RCFs into the pleural (Carthew et al., 1995) or peritoneal (Miller et al., 1999) cavities of rats did not see an increased development of mesothelioma during the lifetime of the exposed rats compared to controls. In the study by Miller et al. (1999), devitrified RCF was the only fibre tested (including two unheated RCFs) that produced no mesotheliomas. Regression analysis suggested that the reason for the difference was that there were fewer long thin fibres in the 'after-service' material than in the unheated fibre samples, which would result in reduced biopersistence (Miller et al., 1999).

Searl et al. (1999) assessed the biopersistence and durability of nine mineral fibres (including RCF-1, RCF-2 and RCF-4) in rat lungs following intratracheal injection of a single 1 mg dose. There were large differences between fibre types in their measured persistence, the 12 month/3 day fibre number ratio, an indicator of fibre clearance, ranging from 7% (for amosite) to 80% (for RCF-4, an after-service fibre) for fibres >0.4 μm in length. For RCF-1 and RCF-2 the corresponding figures were 61% and 69%, respectively. The fibres with the highest proportion of short fibres (amosite and glass fibre) showed the greatest relative reduction in fibre numbers over the 12-month study period. Notwithstanding the fundamentally important influence of fibre length on pulmonary retention, this study suggested that heat-treatment increases RCF biopersistence.

Tomatis et al. (2002) examined the surface properties of three RCFs (kaolin-based ceramic fibre [KBCF]; high-purity fibres; after-service KBCF). The after-service fibres, which had previously been heated at 1300 °C for 24 h and then stored in air, showed the least potential for cytotoxicity and the induction of morphological transformation in Syrian hamster embryo cells. They were also less hydrophilic than un-used KBCFs. Heating the high-purity fibres to 800 °C for 24 h dramatically lowered the amount of water adsorbed and reduced the cytotoxic and transforming potencies of the fibres, compared to untreated fibres, at concentrations between 1 and 16 μg/cm^2. The adsorption capacity of the after-service fibres was about half that of the KBCF and the water was easily removed. The composition of these fibres was not given, although the authors concluded that the state of the surface of RCFs modulates the biological response elicited, and that prolonged thermal treatment transforms RCFs into less hydrophilic materials which have lost the intrinsic potential of the original fibres to damage and transform cells, suggesting that heated fibres are less pathogenic than unheated ones when inhaled. According to the authors, a correlation exists between the degree of surface hydrophilicity and induction of cell damage and transformation; thermal treatment appears, by lowering the surface affinity of RCFs for water, to inhibit some cell-fibre interactions and decrease the extent of internalisation of the fibres.

Brown et al. (1998) assessed the free radical activity (FRA) of MMVFs by measuring plasmid DNA scission, using rat lung lining fluid to coat fibres to determine whether the oxidant-generating ability could be modulated. All fibres showed some degree of FRA, but FRA was only significant in the case of the asbestos positive control. For the MMVFs the FRA ranged from 5% to 20% and was not different from the control (unexposed DNA). The FRA of the heat-treated RCF was slightly lower than the unheated fibre. In addition, hydroxyl radical production was detected for unheated RCF but not for heated RCF. Limited FRA was also observed by Gilmour et al. (1995) following exposure of plasmid ϕX174RF1 DNA to heat-treated RCFs, in contrast to the elevated FRA seen when cells were exposed to asbestos. In an earlier study, Brown et al. (1992) reported the formation of mullite on the surface of heated after-service RCF fibres, with cristobalite formation in the core. This isolation of cristobalite from the surface of the fibres may account for their inability to generate free radicals.

Brown et al. (1992) noted that unheated and heated RCFs showed distinct differences in their interaction with cultured hamster lung cells. Unheated standard grade fibres interacted with cells more rapidly than did unheated high-duty grade fibres; a zirconia grade fibre interacted much less than either. Fibres previously heated to 1200 °C bound to cells to a lesser extent than unheated fibres, and those heated to 1400 °C bound even less, suggesting a progressive reduction in binding with temperature. Cytotoxicity (measured as percentage survival of a murine cell line) of unexposed fibres was much greater than those heated to 1200 °C, which were in turn more toxic than those heated at 1400 °C. Very high fibre concentrations were required to produce detectable levels of arachidonic acid (secondary messenger) release by the cells, and the standard fibre grade was the most active. However, no difference was observed between the unheated and heated fibres at doses between 160 and 1280 μg/cm^2. The heated after-service fibres were shorter and thicker than the unheated fibres, and this was considered to have contributed to their reduced cytotoxicity.

Luoto et al. (1997) measured the ability of various MMVFs – including heated and unheated RCFs – to induce haemolysis in sheep erythrocytes (EH), to release lactate dehydrogenase (LDH) from rat alveolar macrophages and to increase the production of reactive oxygen metabolites (ROM) in human polymorphonuclear leucocytes. The cytotoxicity of the MMVFs was compared with that of quartz and chrysotile asbestos (as positive controls), and TiO_2 (negative control). The cellular toxicity of MMVFs was suggested to be relatively mild and close to that induced by TiO_2, with a modest dose-related increase of EH. EH was greatest for RCF-1 and RCF-3 among the MMVFs but was significantly lower than that for quartz and the other two RCFs. LDH release for the four RCFs was similar to that of TiO_2 and less than 50% of that for quartz. ROM production for RCF-4 (the heat-treated fibre) was similar to chrysotile and less than a third of that for quartz. The authors concluded that RCF-4 showed the lowest toxicity of all fibres. It was also demonstrated to be the least cytotoxic in experiments by Hart et al.

(1992) and Cullen et al. (1997), although Yegles et al. (1995) observed RCF4 to be of intermediate cytotoxicity.

In a series of *in vitro* cytotoxicity and genotoxicity experiments on heated and non-heated AES fibres, Ziemann et al. (2013) similarly showed the CS content to be of minor or no relevance to the intrinsic toxicity of heated AES wools.

In summary, the toxicity of devitrified fibres has been investigated in various *in vitro* tests, including studies on rat, mice, hamster and sheep cells, and a range of end-points analysed including production of ROMs, induction of haemolysis, release of LDH, and FRA. These tests have consistently shown that heat-treated (after-service) fibres are less toxic than unheated fibres.

Studies of health effects in whole animals, most notably those that administered fibres via inhalation or intratracheal injection, have produced similar findings. The validity of studies in which fibres are administered intrapleurally or intraperitoneally is debatable as these methods bypass the body's natural defence mechanisms and do not reflect normal routes of exposure in humans. Inhalation studies are generally regarded as the most reliable for predicting potential health effects of inhaled substances in humans and these have shown that exposure to after-service fibres delays the onset of fibrosis (Rossiter and Chase, 1995) and produces fewer pulmonary neoplasms (no different from controls) (Mast et al., 1995a,b), and also deemed to be the least cytotoxic (Cullen et al., 1997).

Results from studies on biopersistence and biosolubility of fibres are variable, probably due to different methodologies being used and inconsistency in use of the different cell lines and animals. Biopersistence is important because the longer that fibres are retained in the body the greater the chance they have of causing adverse health effects. Two studies that looked at the biopersistence of after-service fibres produced apparently conflicting results (Miller et al., 1999; Searl et al., 1999).

5. Exposure to MMVFs and devitrified components

The primary route of exposure to MMVFs and other dusts produced during their manufacture, processing, installation and removal is inhalation, although there is also the potential for ingestion and dermal contact. Exposure issues, with regard to the products of devitrification, arise especially during the maintenance and removal of after-service material (ASM), for example from furnace linings, with the potential for exposure to MMVFs, CS and other dusts. Removal of ASM may be partial (e.g., prior to repairing damaged material causing a hot spot) or total, and the specific techniques used for removal depend upon the type of MMVF and size of the furnace and thickness of insulation (Gantner, 1986). During removal there is the potential for fibres and dust to be generated and released into the environment where individuals are working.

The HTIW industry is aware of the potential for exposure to ASM and has established a comprehensive Product Stewardship Programme (PSP) to ensure products do not present an unreasonable risk to human health or the environment at any stage of their use. The PSP concerns the entire product life cycle from design, through manufacture and application to disposal of materials, and has established procedures to monitor fibre and dust levels in the industry on a routine basis. In Europe, the industry's 'Controlled and Reduced Exposure' (CARE) programme has been running since 1996 (Maxim et al., 1999).

Utell and Maxim (2010) presented data from the industry's PSP for workers at US plants for the year 2008; indicating TWA fibre concentrations vary with task and job, at both manufacturing and customer plants. Jobs with relatively high concentrations included those involved in removal of RCF (ASM). Similar findings have been observed in Europe (Maxim et al., 1999) with workers involved in the removal of used material again having amongst the highest exposures. If respirators are used by these workers, as recommended by the PSP, potential exposure to fibres/ASM, and consequently cristobalite, other CS and other dusts, would be expected to be significantly reduced.

Various studies have been undertaken on exposure to devitrified MMVFs in a variety of industries. Tests performed on five ceramic fibre-containing insulation blankets or modules that had been removed from heat treat furnaces at a research and development site showed that between 0% and 21% of the bulk fibres had been converted to cristobalite at temperatures in the range of 260–1400 °C (Gantner, 1986). The percentage of cristobalite in corresponding air samples ranged from 4.0% to 14.7%. Analysis of personal samples for respirable dust, taken during the removal of the bonding insulation, indicated a mean concentration of 4.99 mg/m^3 (range: 0.12–16.9 mg/m^3). Further analysis indicated that personal respirable levels reached or exceeded the threshold limit value (TLV) for cristobalite of 0.05 mg/m^3 in about 75% of the samples. In addition, 50% of the personal respirable samples were in excess of the 8 h-TWA for cristobalite, even though the insulation removal only took a short time. Exposure to cristobalite depended on the type of insulation being removed; mean respirable dust concentration for two of the materials was 6.67 and 9.30 mg/m^3, whilst the lowest was 0.47 mg/m^3. However, the exact composition of the various insulation materials was not given; they were said to consist of RCFs, although each had its own form and proprietary bonding agents.

A later study of US refineries and chemical plants during the installation and removal of insulation in furnaces found that the majority of RCF exposures were low (Cheng et al., 1992). However, airborne levels as high as 17 f/cm^3 (means ranging from 0.02 to 1.3 f/cm^3) were observed when removing RCF-containing blankets inside, or when welders cut through crude oil furnace tubes. Furthermore, workers who replaced worn-out RCF modules had exposure to cristobalite in dust samples ranging from 0.03 to 0.2 mg/m^3, with a geometric mean (GM) of 0.06 mg/m^3, marginally above the OSHA established permissible exposure limit (PEL) of 0.05 mg/m^3.

Strubel and Faul (1994) took dust measurements in factories where furnaces containing RCFs were assembled and dismantled. During the process, where fibres had been used for over 2-years at a temperature of 1250 °C, total dust concentrations ranged from 6.38 to 14.98 mg/m^3 (based on only 4 samples); XRD of these samples gave cristobalite contents of up to 20%. They also showed that at 1020 °C (5 cm from the kiln face) the amount of cristobalite exceeded 24% and rose to 30% at the hot face.

Van den Bergen et al. (1994) collected dust samples during the removal of an old RCF lining from a large industrial furnace by pneumatic drilling hammers. During the process, gravimetric measurements showed concentrations of respiratory dust ranging from 9 to 54 mg/m^3 (8 h-TWA), with a GM of 29 mg/m^3. All samples contained a constant 1.5 wt% of quartz. These mean values were significantly greater than the Dutch OELs for respirable dust and quartz; however, the presence of cristobalite could not be detected.

Maxim et al. (1999) reviewed occupational CS exposure in the refractory industries, with particular attention to RCFs, especially the removal of after-service RCFs. Data on 158 samples of after-service fibres, collected as part of the PSP workplace monitoring program over a five-year period, indicated relatively low concentrations of quartz, cristobalite and tridymite. However, due probably to limitations in the sensitivity of the analytical method and the relatively short duration of removal activities, many measurements were below the level of detection (LOD). Only 14 samples had task-time respirable quartz concentrations above their respective LOD; measured values ranged from 0.01 to 0.44 mg/m^3. For cristobalite, only three samples were above their

respective LOD, with a mean value of 0.0178 mg/m^3, below the TLV of 0.05 mg/m^3 (8 h-TWA).

Linnainmaa et al. (2007) assessed exposure to RCFs in two Finnish steel plants, three foundries and a repair shop under normal production and during replacement of oven insulation samples. RCF concentrations were above the OELs (0.2 f/cm^3) during removal of furnace insulation and the maintenance break while removing and installing thermal insulation. However, of the four samples of used insulation with the largest fraction of devitrified fibres that were examined, only one showed the presence of cristobalite, and only as a few percent.

Shih et al. (2008) assessed respirable CS (RCS) exposures to furnace relining workers at a municipal waste incinerator (operating temperature 1000 °C) in Taiwan, during its annual relining period with a "refractory material" (type not specified). There was a large range in RCS exposure between the job-exposure groups (sand-blasting and bottom ash cleaning significantly greater than others) and a large proportion of exposures exceeded the TLV–TWA (0.025 mg/m^3). However, results showed that quartz – probably resulting from the sand-blasting activities – was the only detectable CS content (no cristobalite).

The CARE programme has taken samples in after-service operations to evaluate CS concentrations in addition to fibre levels (ECFIA, 2010). A total of 191 samples were analysed, but only two were above the OEL for quartz and one for cristobalite, with the majority below the LOD for both quartz (165) and cristobalite (185).

In summary, exposure to the products of devitrification occurs only during the repair or removal of after-service fibres in furnace linings, for example. The studies reviewed have indicated a wide range of exposure to respirable quartz and cristobalite, with average levels ranging from 0.01 to 4.99 mg/m^3; in the majority of situations, levels were below the prevailing OEL for the country in which they were measured. A summary of the exposure scenarios and airborne fibre/dust and/or cristobalite concentrations in the above studies is given in Supplementary Table 3.

6. Discussion and conclusions

It is evident from this review that when MMVFs are heated to their working temperature and beyond, there is a degree of devitrification. *In situ* devitrification of HTIW is confined to the surface layers of the insulation, i.e., those near the hot face of the furnace/kiln, where temperatures are greatest, and the amount devitrified decreases with distance from the surface. There is some debate as to exactly when devitrification begins for particular MMVFs, but there is general agreement that the process is both time and temperature dependent. Fibres heated to very high temperatures, well above their normal use temperature, will be devitrified after short periods of time. Fibres heated for long periods to temperatures at or below their typical use temperatures can also show a degree of devitrification.

Because devitrification can result in the production of cristobalite and other CS species, there is some concern about the potential health effects of exposure to heated (after-service) fibres (Gantner, 1986; Comodi et al., 2010), especially as CS is classified by IARC as a Group 1 carcinogen and is known to increase the incidence of non-malignant respiratory disease. However, experimental studies on heated fibres have consistently shown them to be less, not more, toxic than unheated fibres. It has been suggested that the CS produced through the process of devitrification may be toxicologically inactive since it is not available on the surface of the fibre but contracts from the surface during devitrification (Brown et al., 1992; Harrison and Brown, 2011), and is enclosed in the bulk within a predominantly mullite surface coating (Gaodu et al., 1977). In addition, it is postulated that the aluminium in RCFs may inactivate any toxic effect of the silica – a phenomenon that has been known for many decades (Brown et al., 1992; Harrison and Brown, 2011). However, this suggestion is not supported by the similar inactivity observed with devitrified AES fibres, which contain little or no aluminium. The crystallisation process is reported to weaken fibres (Gaodu et al., 1977) and to result in fibre structure collapse (Dietrichs and Kronert, 1981), and this in-service collapse of fibre structure would likely also act to reduce any carcinogenic potential associated with these materials.

It was observed during this review that there was little or no consistency between the studies with regard to the temperatures to which fibres had been heated or the lengths of time that they were exposed to various temperatures. Even within the same study, the range of temperature and timings varied between the fibre types studied. In addition, there was no consistency as to the rate at which the fibres are heated, a factor that may also have an influence on the devitrification process. Also it is not clear from any of the laboratory-based studies on heated fibres whether the temperatures were continuously maintained for the whole time period. For example, in the study by Laskowski et al. (1994), it is not apparent whether temperatures of 1200 and 1300 °C were maintained continuously for the full 7300 h (301 days). The classification temperatures of the various fibres are often not given, let alone the continuous use temperature, and some of the temperatures used in the studies would almost certainly have been above these recommended values.

The preparation of material prior to XRD analysis may have had some influence on the results. In most cases, samples were ground or put in a ball mill to create a powder for analysis. It is conceivable that this process may free up the CS that is suggested to be bound in the fibre matrix, allowing more to be detected. This may similarly be important when samples are tested in toxicological studies.

In vitro studies on cells from different species (including hamsters, mice, rat and sheep) have consistently shown heat-treated fibres to be the least toxic. Studies on whole animals have shown similar results for RCF4, the heated after-service' fibre. Intrapleural infusion or intraperitoneal injection studies have not shown an increase in mesothelioma in those animals exposed to RCF4.

In addition to changes in fibre chemistry, the morphology of after-service fibres has been shown to change significantly. Both Comodi et al. (2010) and Gualtieri et al. (2009) showed a decrease in length and changes in other dimensions,[3] known to affect biopersistence. More work is required to characterise such after-service fibres, including changes in their biopersistence.

Exposure to respirable fibres can be elevated during uncontrolled removal operations when the material has become extremely dusty, but such exposures have decreased significantly in recent years (Maxim et al., 1999; ECFIA, 2010). Particular concern has been expressed about CS exposure during the removal of furnace linings (Gantner, 1986), but the present work shows that the CS produced by devitrification may not be available for interaction with biological targets and therefore its presence may not be as important as previously thought (Harrison and Brown, 2011).

Measurements of RCS, especially cristobalite, in the environment during furnace lining removal/repair via static or personal samplers have shown contrasting results. Some have shown levels to be above exposure limits for an 8 h-TWA of 0.5/1 fibre/ml (Gantner, 1986; Cheng et al., 1992; Strubel and Faul, 1994; Sweeney and Gilgrist, 1998; Fairfax and Burmeister, 2001; Shih et al., 2008), whereas others have shown levels to be below this limit (Rice et al., 1994; van den Bergen et al., 1994; Groat et al., 1999; Maxim et al., 2008; Linnainmaa et al., 2007). However, all these results

[3] Reported also by Ziemann et al. (2013).

assume that the worker would not be wearing respiratory protective equipment (RPE), which is advisable to anyone involved in the removal of after-service fibres to prevent exposure to elevated levels of airborne dust.

7. Recommendations

This review indicates that there are some gaps in our knowledge about the devitrification of MMVFs, the toxicity of after-service MMVFs, and the potential exposure to cristobalite in workers in the various industries that use MMVFs, especially those involved in their repair/removal. As a consequence there are a number of recommendations for further work:

- Further detailed studies on the chemico-physical processes of devitrification of different fibre types, using standard times and temperatures and different rates of heating, to better define the temperature threshold for CS formation. This should, where possible, be undertaken in a way that resembles normal use conditions, including the use of firing cycles.
- Further characterisation of untreated and devitrified fibres in terms of length and diameter.
- Investigations into whether devitrified fibres are more easily removed from the lungs, as a consequence of the hypothesis that they break and are cleared more quickly than other fibres.
- Further studies of the cytotoxicity and biopersistence of devitrified fibres. Numerous studies have been undertaken on rat lung macrophages *in vitro*, but it would also be appropriate to use human cell lines, if possible, investigating a variety of endpoints. Additional inhalation studies on heated MMVF would be useful.
- Identification, measurement and micro-location of CS within the matrix of devitrified fibres since, in devitrified fibres, the crystalline silica is believed to be trapped in grain boundaries between a matrix predominantly consisting of other crystal formations (mixed minerals) or glass (ECFIA, 2010) and it would be useful to demonstrate this.
- Further studies to assess the bioavailability of cristobalite, and other high-temperature CS forms in devitrified fibres, and investigate whether the aluminium in RCFs deactivates any toxicological effect (Harrison and Brown, 2011).
- Although exposure levels appear to be low, monitoring of respirable dust, quartz and cristobalite levels should be encouraged during operations when contact with after-service fibres is possible and workers should be obliged to wear the correct RPE.

Conflicts of interest

One of the authors (P.T.C. Harrison) acts as a consultant to ECFIA, an association representing the HTIW industry, in matters relating to health and safety, but he is not involved in any legal testimony related to the materials in questions nor does he have any other commercial interest in these materials.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.yrtph.2013.11.014.

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